

# Grey, brown and blue coloring sol gel electrochromic devices

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## Abstract

Pure and doped niobium oxide ( $\text{Nb}_2\text{O}_5$ ) layers are electrochromic (EC) materials which change their color by insertion of  $\text{Li}^+$  ions from transparent to brown, grey or blue depending on the crystallinity of the layer. EC devices with the configuration K glass/EC layer/composite electrolyte/ion storage (IS) layer/K glass, were produced using different  $\text{Nb}_2\text{O}_5$  EC layers, a  $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$  ( $x \approx 0.45$ ) IS layer and an inorganic-organic composite electrolyte to which a small amount of water (up to 3 wt.%) was added. The grey coloring all solid state sol gel devices fabricated with  $\text{Nb}_2\text{O}_5:\text{Mo}$  coatings show a high reversible coloration ( $\Delta\text{OD} \approx 0.3$ ) and a long term stability of more than 55 000 switching cycles. Large area EC devices ( $30 \times 40$  cm) show a transmittance change between 60% and 25% at 550 nm after galvanostatic coloration and bleaching for 3 min and a coloration efficiency of  $27 \text{ cm}^2/\text{C}$ . The results obtained with blue and brown coloring  $\text{Nb}_2\text{O}_5$  EC layers and a comparison with blue coloring  $\text{WO}_3$  layers are also presented.

**Keywords:** Electrochromic device; Smart window; Niobium oxide; Sol gel; Water content

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## 1. Introduction

Electrochromic (EC) windows, also called “smart windows”, change their optical properties (transmittance or reflection) in a reversible manner when a voltage is applied and a current flows through them [1,2]. They are of considerable interest for architectural and automotive applications in order to control the solar radiation entrance and to save costs for air conditioning. A typical configuration of EC-devices made with the sol-gel process (and used in this report) is glass/FTO (fluorine doped tin oxide,  $\text{SnO}_2:\text{F}$ )/EC-layer/solid composite electrolyte/ $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$  (ion-storage layer)/FTO/glass.

Because of their high coloration efficiency, the  $\text{WO}_3$  EC-layers are the most studied coatings and have been prepared by many processes [1,3,4]. The colored devices present a dark blue color.

$\text{Nb}_2\text{O}_5$  based coatings are also promising EC electrodes and have been also prepared by many processes [1,3,5–11]. However devices made with these coatings were not successful and suffered from the small coloration efficiency

of niobia coatings and their fast degradation under cycling [8,9]. One of the advantages of niobia coatings is the possibility to obtain different colors varying from brown for amorphous layers, grey for crystalline layers with small crystallite sizes ( $<25$  nm) and blue for those with large crystallite sizes ( $>30$  nm) [7–9]. The doping of the layers also influences the crystallite size and therefore the coloration.

The disadvantage of the  $\text{Nb}_2\text{O}_5$  layers is their small coloration efficiency (CE) of about  $15\text{--}27 \text{ cm}^2/\text{C}$  in comparison to that of tungsten oxide ( $\text{CE}=37\text{--}50 \text{ cm}^2/\text{C}$  [1,2]) and until now their use was precluded for the realization of deep coloring EC windows as the reversible  $\text{Li}^+$  ion-storage (IS) capacity of the available IS layer was too low.

Recently we showed that the ion-storage capacity of  $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$  ion-storage layers could be improved from 3 to  $11 \text{ mC}/\text{cm}^2$  by addition of small amounts of water (up to 3 wt.%) to an electrolyte consisting of 1 M  $\text{LiClO}_4$  in propylene carbonate [12]. The addition of water to the inorganic-organic composite electrolyte of EC-devices with electrochromic sol-gel  $\text{WO}_3$  layers also improved the transmittance change and the long-term stability of the EC-devices up to 50 000 switching cycles [12,13]. This gave the impulse to prepare EC-devices of the configuration K-

glass/Nb<sub>2</sub>O<sub>5</sub>/inorganic–organic composite electrolyte/(CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1–x</sub> (ion-storage layer)/FTO/glass with addition of small amounts of water to the composite electrolyte and to study the electrochromic properties of the devices.

In this report the electrochromic properties of different electrochromic Nb<sub>2</sub>O<sub>5</sub> layers and of EC-devices of the above configuration are presented.

## 2. Experimental

### 2.1. Sols and coatings

A 0.4 M niobium solution was prepared by dissolving NbCl<sub>5</sub> (ChemPur) in ethanol and acetic acid. The doping was obtained by dissolving either 12-molybdophosphoric acid (H<sub>3</sub>[P(Mo<sub>3</sub>O<sub>10</sub>)<sub>4</sub>], Fluka) (molar ratio Mo:Nb=0.3) or LiCF<sub>3</sub>ClO<sub>4</sub> (molar ratio Li:Nb=0.1) in ethanol. Both solutions were mixed and then submitted to an ultrasonic treatment for 2 min [7–9]. The (CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1–x</sub> sol ( $x=0.45$ ) was prepared by dissolving Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O (0.056 mol) and Ti(O<sup>i</sup>Pr)<sub>4</sub> (0.069 mol) in 250 ml ethanol followed by stirring the sol at 30 °C for 4 days [12].

The solid ionic conductor is based on glycidoxypropyl-trimethoxysilane (GPTS), LiClO<sub>4</sub>, Zr(O<sup>n</sup>Pr)<sub>4</sub> and tetraethylene glycol (TEG) and its preparation was described elsewhere [14,15].

The K-glass substrates (glass coated with FTO, Pilkington, 17 Ω<sub>□</sub>) were washed, dried and heat treated at 450 °C for 15 min.

The grey coloring Nb<sub>2</sub>O<sub>5</sub>:Mo sol–gel coatings were deposited on these substrates by the dip-coating technique with a withdrawal rate of 2 mm/s at 20 °C with 38% air humidity. The films were dried at 100 °C and then heat treated at 500 °C for 30 min. The whole procedure was repeated one time to increase the thickness of the coating.

The brown coloring Nb<sub>2</sub>O<sub>5</sub>:Li and the blue coloring Nb<sub>2</sub>O<sub>5</sub> sol–gel coatings were deposited on K-glass by the dip-coating technique with a withdrawal rate of 4 mm/s under the same experimental conditions. The films were dried at 250 °C for 30 min and then heat treated for 30 min at 400 °C for Nb<sub>2</sub>O<sub>5</sub>:Li and at 500 °C for Nb<sub>2</sub>O<sub>5</sub> coatings, respectively. The whole procedure was repeated one time to increase the thickness of the coating.

The (CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1–x</sub> layers were deposited in a single coating step on K-glass by the dip-coating technique with a withdrawal rate of 4 mm/s under the same experimental conditions. The single layers were then heated in air at 450 °C with a heating rate of 2.5 K/min, kept for 15 min at 450 °C and then cooled down to room temperature in the oven within 5 h. To increase the thickness of the coating, the whole procedure was repeated one time.

The EC-devices (size 5 × 10 to 30 × 40 cm<sup>2</sup>) with the configuration K-glass/EC-layer/inorganic–organic composite electrolyte/(CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1–x</sub>/K-glass were built by mounting a double sided adhesive tape (thickness 1 mm,

3 M) at the edges of one of the functional coatings and then assembling the two coated substrates as described elsewhere [16]. The mounted cells were then filled with the liquid inorganic–organic composite electrolyte through a small hole, heated at 105 °C for 12 h to solidify the electrolyte and then extra sealed using butyl rubber (3 M) and adhesive tape. Devices were made with and without adding 3 wt.% water to the electrolyte before filling the cells.

### 2.2. Characterization of coatings and devices

The layer thickness was determined by scratching the layers before the heat treatment and subsequently measuring the step height with a TENCOR P-10 surface profiler.

The coatings were studied electrochemically in a three electrode cell using a platinum sheet as counter electrode, a Ag/AgClO<sub>4</sub> reference electrode (0.01 M AgClO<sub>4</sub> in 1 M LiClO<sub>4</sub> in propylene carbonate (PC)) and a liquid electrolyte consisting of 1 M LiClO<sub>4</sub> in propylene carbonate (PC) without or with 3 wt.% added water. The water content of the liquid electrolyte was determined by Karl–Fisher titration. The working electrode (size 4 × 9 cm<sup>2</sup>) was pressed against a silicone O-ring on one side of the three electrode cell. The electrochemical area was 7 cm<sup>2</sup>.

The electrochemical measurements were performed using an EG&G 273A potentiostat. The samples were studied by Chronoamperometric (CA) measurements using a potential range of –2.2 to +1.0 V for Nb<sub>2</sub>O<sub>5</sub>:Mo, Nb<sub>2</sub>O<sub>5</sub>:Li and Nb<sub>2</sub>O<sub>5</sub> coatings and a range of –2.5 to +1.5 V for EC-devices with Nb<sub>2</sub>O<sub>5</sub>:Mo and –2.5 to +2.5 V for EC-devices with Nb<sub>2</sub>O<sub>5</sub>:Li and Nb<sub>2</sub>O<sub>5</sub> as EC-layer. The potentials were applied for 120 s, respectively. This lapse of time was chosen to obtain data in a reasonable experimental time (typically 10 000 cycles in 30 days). As will be shown below, the lapse of time for each cycle does not always allow a full intercalation of the layers but is sufficient for a full deintercalation. It is nevertheless convenient for comparison purposes.

In situ transmittance measurements were carried out with a CARY 5E UV/VIS/NIR spectrophotometer. The transmittance of the Nb<sub>2</sub>O<sub>5</sub>:X coatings was measured in the electrochemical cell against a reference cell having a quartz glass and a float glass window. The transmittance of the EC-devices was measured against air as a reference.

Structural characterization of the coatings were performed using an X-ray diffractometer (Siemens D500) and a high resolution transmission electron microscope HR-TEM (Philips CM200-FEG).

## 3. Results and discussion

### 3.1. Material characterization

The thickness of the Nb<sub>2</sub>O<sub>5</sub>:X double layers was 120 nm for Nb<sub>2</sub>O<sub>5</sub>:Mo, 225 nm for Nb<sub>2</sub>O<sub>5</sub>:Li and 170 nm for

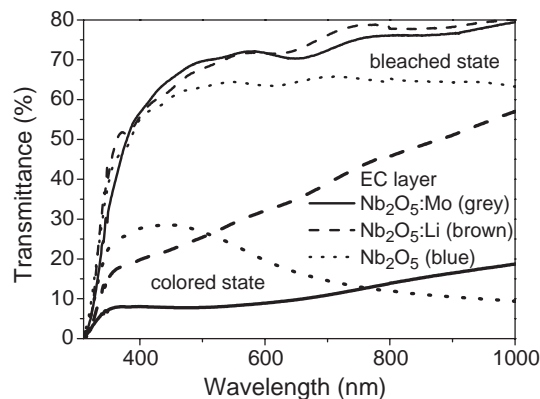


Fig. 1. Transmittance spectra of undoped and doped Nb<sub>2</sub>O<sub>5</sub>:X sol gel double layers on K-glass, sintered at different temperatures, in the colored and bleached state measured in 1 M LiClO<sub>4</sub> in PC (-2.2 V vs. Ag/AgClO<sub>4</sub>, 2 min/+1 V, 2 min).

Nb<sub>2</sub>O<sub>5</sub>. The thickness of the (CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1-x</sub> was 200 nm for the single layers and 400 nm for the double layers. The water content of the “dry” liquid electrolyte was 0.03 wt.%. X-ray diffraction spectra indicate that the Nb<sub>2</sub>O<sub>5</sub>:Mo layer was crystalline. The structure does not correspond to the hexagonal form of pure Nb<sub>2</sub>O<sub>5</sub> obtained after heat treatment at 500 °C (JCPDS file 28-317) [7–9]) but most of the diffraction peaks can be indexed either as a monoclinic Nb<sub>2</sub>O<sub>5</sub> (JCPDS 37-1468) or orthorhombic Nb<sub>12</sub>O<sub>29</sub> (JCPDS 34-1169). The size of the crystallites cannot be determined with precision. The Nb<sub>2</sub>O<sub>5</sub>:Li and the (CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1-x</sub> layers were X-ray amorphous. TEM micrographs showed also that the (CeO<sub>2</sub>)<sub>x</sub>(TiO<sub>2</sub>)<sub>1-x</sub> layer is amorphous.

### 3.2. Electrochemical characterization

#### 3.2.1. EC layers

The transmittance spectra of different Nb<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>:X sol-gel double layers deposited on K-glass in the bleached and colored state are shown in Fig. 1 (50th

switching cycle). After sintering up to 450 °C, the amorphous Nb<sub>2</sub>O<sub>5</sub>:Li layers color brown after intercalation of Li<sup>+</sup> ions. Undoped Nb<sub>2</sub>O<sub>5</sub> layers, sintered at 500 °C or at higher temperatures are crystalline and color blue after Li<sup>+</sup> ion intercalation. Molybdenum doped Nb<sub>2</sub>O<sub>5</sub> layers color grey after Li<sup>+</sup> ion insertion, even after sintering at 500 °C, in agreement with Schmitt and colleagues [7–9].

The transmittance of grey, brown and blue coloring Nb<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>:X (X=Mo, Li) double layers, respectively, at the wavelength of 550 nm after potentiostatic switching in electrolyte (1 M LiClO<sub>4</sub> in PC) without and with addition of 3 wt.% of water is shown in Fig. 2 as a function of the CA-cycle number.

For Nb<sub>2</sub>O<sub>5</sub>:Mo double layers (120 nm thick), the transmittance of the bleached and colored state remains constant from the first cycles up to 3500 cycles and the difference  $\Delta T$  is about 63%. With 3 wt.% water, the transmittance of the bleached state continuously decreases and that of the colored state continuously increases up to the 2000th cycle where the difference stabilizes to 20%.

For brown coloring Nb<sub>2</sub>O<sub>5</sub>:Li double layers (225 nm thick), the transmittance change ( $\Delta T$ ) is smaller than for Nb<sub>2</sub>O<sub>5</sub>:Mo double layers in spite of the higher thickness of the layer.  $\Delta T$  of the brown layers increases in dry electrolyte with the CA cycle number from 26% up to 42% after 50 CA cycles and remains constant up to 300 CA cycles. In wet electrolyte it decreases from 58% down to 36% after 300 CA cycles. Thus the electrochromic behaviour in wet electrolyte is worse than in dry electrolyte for both layers.

The transmittance change of blue coloring Nb<sub>2</sub>O<sub>5</sub> layers in dry electrolyte increased only slightly from 39% to 41% from the first to the 50th cycle.

The time evolution of the normalized transmittance ratio  $T/T_{\text{bleached}}$  of Nb<sub>2</sub>O<sub>5</sub>:Mo and Nb<sub>2</sub>O<sub>5</sub>:Li and Nb<sub>2</sub>O<sub>5</sub> layers measured at 550 nm during the 300th CA cycle (50th for Nb<sub>2</sub>O<sub>5</sub>) is shown in Fig. 3. The coloration and bleaching kinetics are much faster without water in the electrolyte.

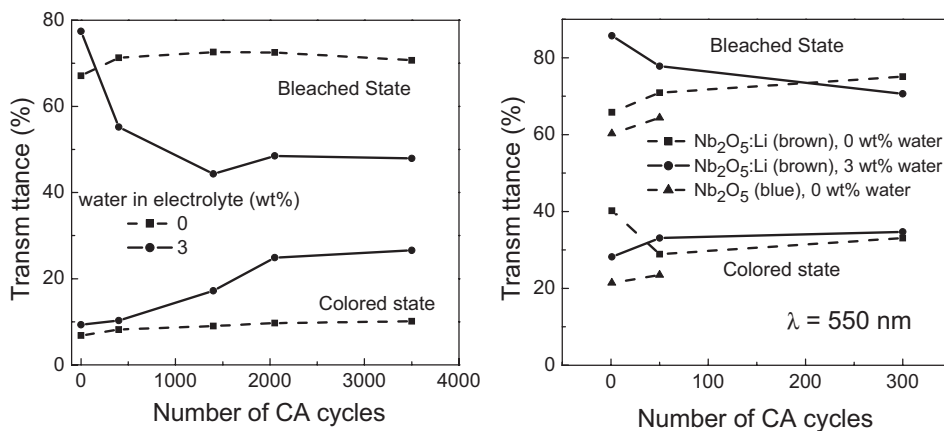


Fig. 2. Transmittance of Nb<sub>2</sub>O<sub>5</sub>:Mo (grey coloring, 120 nm thick, left side), Nb<sub>2</sub>O<sub>5</sub>:Li (brown coloring, 225 nm thick, right) and Nb<sub>2</sub>O<sub>5</sub> (blue coloring, 170 nm, right) sol gel double layers as a function of the CA cycle number (-2.2 V vs. Ag/AgClO<sub>4</sub>, 2 min/+1 V, 2 min) with 0 and 3 wt.% water added to the liquid electrolyte (1 M LiClO<sub>4</sub> in PC) (wavelength 550 nm).

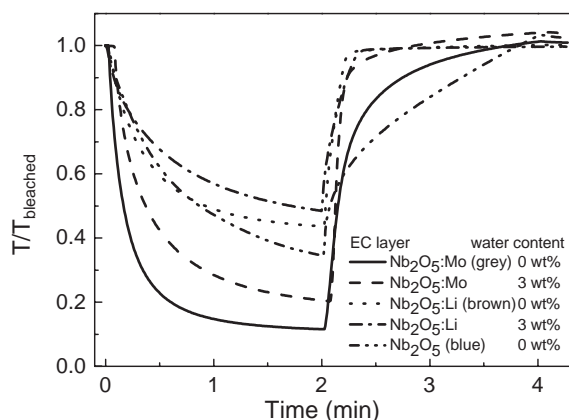


Fig. 3. Time evolution of the normalized transmittance  $T/T_{\text{bleached}}$  of  $\text{Nb}_2\text{O}_5:\text{Mo}$ ,  $\text{Nb}_2\text{O}_5:\text{Li}$  and  $\text{Nb}_2\text{O}_5$  sol gel layers at  $\lambda = 550$  nm during the 300th CA cycle number (50th for  $\text{Nb}_2\text{O}_5$ ) ( $-2.2$  V, 2 min/+1.0 V, 2 min) with 0 and 3 wt.% water added to the liquid electrolyte (1 M  $\text{LiClO}_4$  in PC).

### 3.2.2. EC devices

The electrooptical properties of EC-devices of the configuration glass/FTO/ $\text{Nb}_2\text{O}_5:\text{X}$ /solid composite electrolyte/ $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ /FTO/glass were studied with and without addition of 3 wt.% water to the inorganic–organic composite electrolyte. The effect of the water addition to the composite electrolyte depends on the EC-layer. For grey coloring EC-devices ( $\text{Nb}_2\text{O}_5:\text{Mo}$  layer), the transmittance change is slightly increased by addition of water to the electrolyte (Fig. 4), and this is due to the faster kinetic in the wet electrolyte (Fig. 5). For EC-devices with brown coloring  $\text{Nb}_2\text{O}_5:\text{Li}$  layers the contrary is observed. The transmittance change is smaller with wet electrolyte, due to the slower kinetic (Fig. 5). The color of the windows is not as brown as that of the EC-layers measured in the liquid electrolyte (Fig. 1). The windows color greyish-brown because of the combination of the brown EC layer with the yellowish color of the  $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$  ion-storage layer in the EC-device. EC-devices with blue coloring  $\text{Nb}_2\text{O}_5$  layers were only studied with wet composite electrolyte and showed a transmittance change of 14%

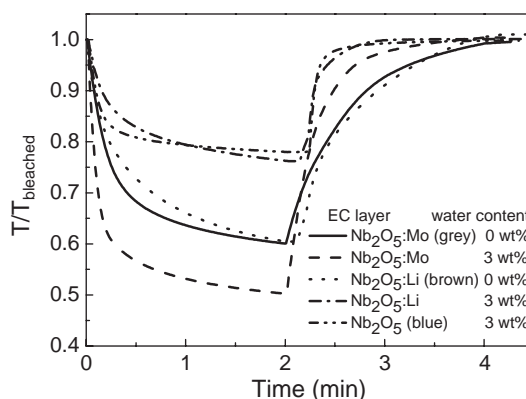


Fig. 5. Normalized transmittance,  $T/T_{\text{bleached}}$  ( $\lambda = 550$  nm), versus time of EC-devices with  $\text{Nb}_2\text{O}_5:\text{X}$  EC layer without and with addition of 3 wt.% water in the inorganic–organic composite electrolyte during the 2000th CA (X Li) and 8000th (X Mo) CA cycle ( $-2.5$  V, 2 min/+1.5 (X Mo), 2.5 V (X Li), 2 min).

(Fig. 4, right side), which is smaller than that of EC-devices with blue coloring  $\text{WO}_3$  layers ( $\Delta T = 40\%$  [12,13,16]).

The change of the optical density at 550 nm as a function of the CA cycle number is shown in Fig. 6. For grey coloring EC-devices with  $\text{Nb}_2\text{O}_5:\text{Mo}$  layers, drastic variations are observed without water (Fig. 6, left side). During the initial cycling  $\Delta\text{OD}$  is small (about 0.1), increases continuously to about 0.33 up to 700 cycles and then decreases down to 0.1 after 14000 cycles when the cell is destroyed. This variation is considerably reduced by adding water in the electrolyte. For 3 wt.% water,  $\Delta\text{OD}$  is higher at the first cycle (about 0.2), increases up to 0.31 (700th–2000th CA cycle) and then only slightly decreases up to 55000 cycles. This slight variation is due to a kinetic effect, because after applying  $-2.5$  V for 4 min (instead of 2 min, see Fig. 6, left side) the same high value of the optical density ( $\Delta\text{OD} = 0.31$ ) is reached. The window is therefore fully stable.

For EC-devices with brown coloring  $\text{Nb}_2\text{O}_5:\text{Li}$  layers, the behaviour is different (Fig. 6, right side): in dry electrolyte,  $\Delta\text{OD}$  increases from 0.1 to 0.22 after 1000

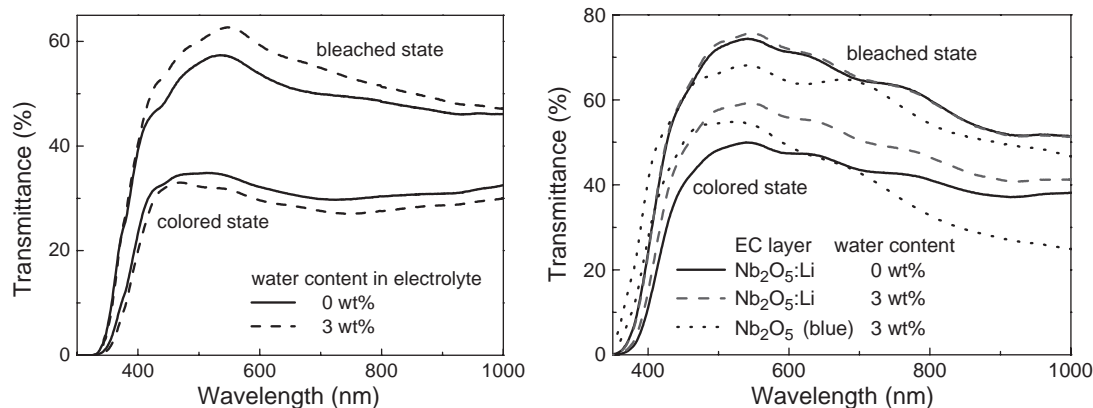


Fig. 4. Transmittance of EC-devices with the configuration glass/FTO/ $\text{Nb}_2\text{O}_5:\text{X}$ /composite electrolyte/ $(\text{CeO}_2)_x(\text{TiO}_2)_{1-x}$ /FTO/glass in the colored ( $-2.5$  V, 2 min) and bleached ( $+1.5$  V, 2 min, X Mo, left side,  $+2.5$  V, 2 min, X Li and  $\text{Nb}_2\text{O}_5$ , right side) state without and with addition of 3 wt.% water in the inorganic–organic composite electrolyte.

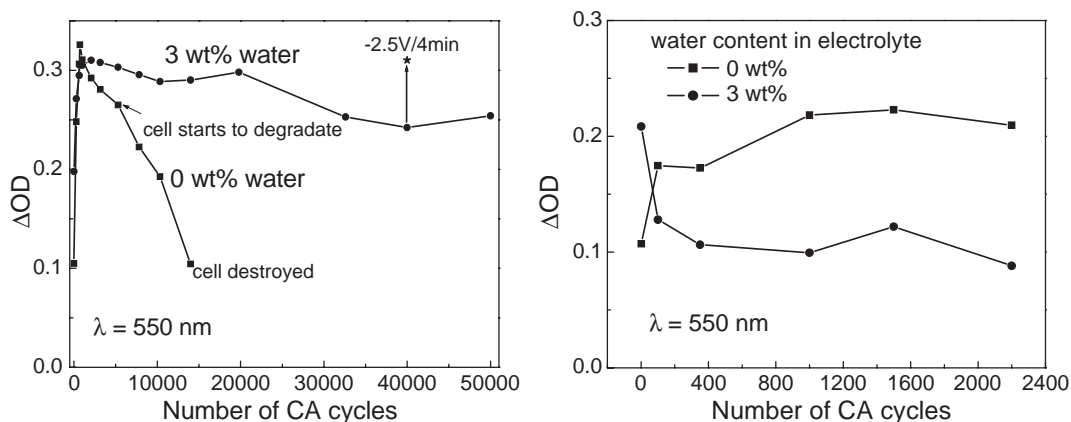


Fig. 6. Change of the optical density  $\Delta OD$  at  $\lambda = 550$  nm of EC-devices with the configuration K-glass/ $Nb_2O_5:X$ /composite electrolyte/ $(CeO_2)_x(TiO_2)_{1-x}$ /K-glass without and with addition of 3 wt.% water in the electrolyte as a function of the CA cycle number ( $-2.5$  V, 2 min/ $+1.5$  V, 2 min, X Mo, left side,  $+2.5$  V, 2 min, X Li, right side).

cycles and then remains constant, whereby only 2200 cycles were tested until now. In electrolyte with 3 wt.% water,  $\Delta OD$  decreases from 0.21 to 0.1 after 300 cycles and then remains rather constant up to 2200 cycles. The  $\Delta OD$  of the greyish brown coloring windows is much smaller than that of the grey coloring devices.

The coloration efficiency of the grey coloring EC-devices with wet electrolyte is  $27 \text{ cm}^2/\text{C}$  from the 2000th up to the 50 000th cycle. The coloration efficiency of the EC-devices with brown coloring  $Nb_2O_5:Li$  EC layer is  $23 \text{ cm}^2/\text{C}$  for EC-devices with dry electrolyte and  $28 \text{ cm}^2/\text{C}$  for EC-devices with wet electrolyte, which is similar to the grey coloring windows. Cycling tests are still going on in order to determine the long-term stability of the devices.

The  $\Delta OD$  of the blue coloring windows with  $Nb_2O_5$  layers was 0.1 with 3 wt.% water in the composite electrolyte, which is much smaller than that observed for EC-devices with blue coloring  $WO_3$  layers ( $\Delta OD = 0.36$  [12,13]). The coloration efficiency (CE) of the blue window with  $Nb_2O_5$  was  $22 \text{ cm}^2/\text{C}$  and therefore smaller than the CE of brown and grey coloring EC-devices.

The highest transmittance change of the described layers was obtained with the grey coloring  $Nb_2O_5:Mo$  EC-layers. Therefore large area EC-devices ( $30 \times 40 \text{ cm}^2$ ) were built

with this EC-layer (Fig. 7). They show a transmittance change between 60% and 25% at 550 nm after galvanostatic coloration and bleaching for 3 min. The coloration efficiency for the above cell is around  $27 \text{ cm}^2/\text{C}$ .

#### 4. Conclusion

Grey, brown and blue coloring  $Nb_2O_5:X$  EC-layers were studied in liquid electrolyte and in EC-devices with the configuration K-glass/EC-layer/composite electrolyte/ $(CeO_2)_x(TiO_2)_{1-x}$ /K-glass without and with addition of water to the electrolyte. The behaviour of the EC-layers and EC-devices with the water content of the electrolyte is different. The highest  $\Delta OD$  of 0.3 was obtained with grey coloring EC-devices with  $Nb_2O_5:Mo$  EC-layers and 3 wt.% water addition to the composite electrolyte, which showed a long-term stability of more than 55 000 switching cycles. The EC-devices with the brown coloring  $Nb_2O_5:Li$  EC-layers color greyish brown and have a higher  $\Delta OD$  ( $\Delta OD = 0.22$ ) in dry electrolyte. Blue EC-devices have a  $\Delta OD$  of 0.1 in wet electrolyte which is much smaller than that of EC-devices with  $WO_3$  as EC-layer (0.36). The long-term stability of grey coloring EC-devices with  $Nb_2O_5:Mo$

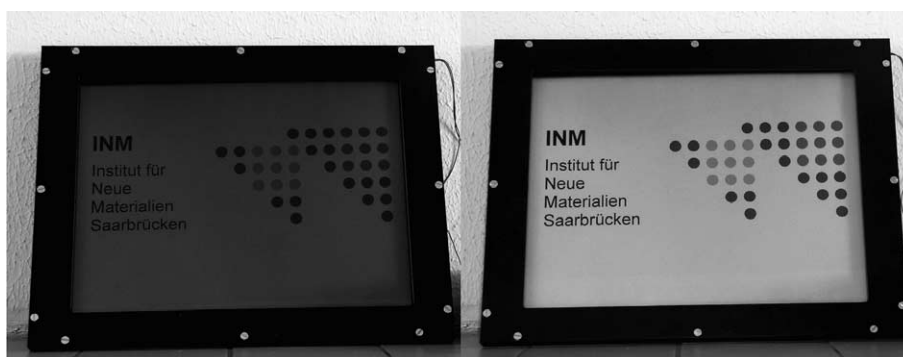


Fig. 7. Large area grey coloring EC window ( $30 \times 40 \text{ cm}^2$ ) in the colored and bleached state after galvanostatic coloration (transmittance at 550 nm: 25%) and bleaching (60%) for 3 min.



EC layers could be drastically improved by the addition of water to the composite electrolyte. Further studies are underway to study the long-term stability of the brown and blue EC-devices.

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